

KOKAI PATENT APPLICATION NO. HEI 7-215708

**COMPLEX OF HYDRAZINE, SOLID SOLUTION POWDER MADE OF COMPLEX OF
HYDRAZINE, ALUMINA-ZIRCONIA POWDER MATERIAL, ALUMINA-ZIRCONIA
CERAMIC BODY, ALUMINA-ZIRCONIA GRIT AND MANUFACTURING METHOD
FOR THESE**

[Translated from Japanese]

[Translation No. LPX20356]

Translation Requested by: Paul Davies 3M

Translation Provided by: Yoko and Bob Jasper
Japanese Language Services
16 Oakridge Drive
White Bear Lake, MN 55110

(651) 426-3017 Fax (651) 426-8483
e-mail: bjasper@attbi.com

JAPANESE PATENT OFFICE (JP)

PATENT JOURNAL (A)

KOKAI PATENT APPLICATION NO. HEI 7-215708

Technical Indication Section

Int. Cl.⁶:

C 01 B 21/16
B 24 B 7/22
37/00
B 24 D 3/00
G 01 F 17/00
G 01 G25/00
G 04 B 35/10

Identification Code:

Z
H
E

Sequence Nos. for Office Use:

FI

Filing No.:

Hei 6-7355

Filing Date:

January 27, 1994

Publication Date:

August 15, 1995

No. of Claims:

9 OL (Total of 6 pages in the [Japanese] document)

Examination Request:

Not filed

COMPLEX OF HYDRAZINE, SOLID SOLUTION POWDER MADE OF COMPLEX OF HYDRAZINE, ALUMINA-ZIRCONIA POWDER MATERIAL, ALUMINA-ZIRCONIA CERAMIC BODY, ALUMINA-ZIRCONIA GRIT AND MANUFACTURING METHOD FOR THESE

[*Hidoragin no sakukagohbutsu, hidoragin no sakukagohbutsu o mochiita kyooh tai function'matsu, arumina-girukoniakei fun'tai zairyoh, arumina-girukoniakei seramikkustai, arumina-girukoniakei toryuh, oyobi korerano seizoh houhoh*]

Inventor(s):

Masahiro Tamamaki
c/o Japan Abrasive
Co., Ltd.
90 banchi, Kita-machi
Ishizu, Sakai-shi
Osaka-fu

Sohichi Fujii
c/o Japan Abrasive
Co., Ltd.
90 banchi, Kita-machi
Ishizu, Sakai-shi
Osaka-fu

Kohji Tsuda
c/o Japan Abrasive
Co., Ltd.
90 banchi, Kita-machi
Ishizu, Sakai-shi
Osaka-fu

Applicant(s):

390002082
Japan Abrasive
Co., Ltd.
90 banchi, Kita-machi
Ishizu, Sakai-shi
Osaka-fu

Agent(s):

Yasuo Ohshima
Patent attorney
and 1 other

[Translator's note: Names of products and companies are spelled phonetically in this translation.]

[Translator's note: The format of the document supplied by the requester has been changed from the original Japanese Patent Application submitted by the applicant to accommodate machine translation.]

[Abstract] (Rewritten)

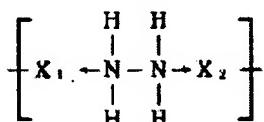
[Purpose] The purpose of the present invention is to produce a fine alumina-zirconia powder material having a uniform distribution of components and high bonding strength, an alumina-zirconia ceramic body having high strength and high toughness, alumina-zirconia grit with high grinding performance, and a hydrazine complex useful for production of these, and to provide a manufacturing method for these.

[Constitution] A complex made of a two-nuclei complex formed by coordinate bonding of hydrazine and aluminum, zirconium, or yttrium, a solid solution powder produced by pulverizing and calcinating the aforementioned complex, alumina-zirconia powder material produced by heating the aforementioned solid solution powder, alumina-zirconia ceramic body produced by die molding the aforementioned alumina-zirconia powder material followed by HIP treatment, and alumina-zirconia grit produced by pulverizing, calcinating, and baking the complex.

[Claim of the invention]

[Claim 1] A complex comprising a two-nuclei complex produced by coordinate bonding of hydrazine shown in the following general formula

[Chemical formula 1]

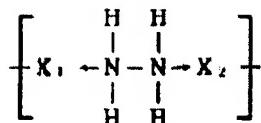


Wherein, X_1 and X_2 are Al, Zr, or Y

and aluminum, zirconium, or ytterbium.

[Claim 2] A method of manufacturing a complex produced by coordinate bonding of hydrazine shown in the following general formula

[Chemical formula 2]



Wherein, X_1 and X_2 are Al, Zr, or Y

prepared by adding hydrazine to an aqueous solution of halide of aluminum and zirconium or a halide of ytterbium under stirring
and aluminum, zirconium, or ytterbium.

[Claim 3] A solid solution powder produced by pulverizing the complex described in claim 1 and calcinating in an oxidizing atmosphere at a temperature of 300°C or above.

[Claim 4] A solid solution powder produced by heat-treatment of the solid solution powder described in claim 3 at a temperature in the range of 900°C to 1300°C.

[Claim 5] An alumina-zirconia ceramic body produced by die molding and HIP treatment of the alumina-zirconia powder material described in claim 4.

[Claim 6] An alumina-zirconia grit produced by pulverizing the complex described in claim 1, calcinating in an oxidizing atmosphere at a temperature of 300°C or above, and baking at a temperature in the range of 1350 to 1600°C.

[Claim 7] A method of manufacturing an alumina-zirconia powder material characterized by the fact that drying, pulverizing and calcinating are performed for the water-washed complex produced by the reaction of a halide of aluminum, zirconium and ytterbium calculated to form a mixing ratio of 95 to 50 mol% of Al_2O_3 , 5 to 50 mol% of ZrO_2 and 1 to 3 mol% of Y_2O_3 for ZrO_2 as a final product with hydrazine in a liquid phase, and a heat-treatment is further applied at a temperature in the range of 900°C to 1300°C.

[Claim 8] A method of manufacturing an alumina-zirconia ceramic body characterized by the fact that classification is performed for the alumina-zirconia powder material produced by the method described in claim 7, die molding is performed and HIP treatment is further performed.

[Claim 9] A method of manufacturing alumina-zirconia grit characterized by the fact that

drying, pulverizing, and calcinating are provided for a water-washed complex produced by the reaction of a halide of aluminum, zirconium, and ytterbium calculated to form a mixing ratio of 95 to 50 mol% of Al_2O_3 , 5 to 50 mol% of ZrO_2 and 1 to 3 mol% of Y_2O_3 for ZrO_2 as a final product with hydrazine in a liquid phase, and baking is further performed at a temperature in the range of 1350°C to 1600°C.

[Detailed description of the invention]

[0001]

[Field of industrial application] The present invention pertains to an alumina-zirconia powder material used for cutters such as cutting tools with high strength and high toughness, crushing media such as balls, and machine parts such as bearings, fine powder abrasives and grind stone for lapping and polishing, alumina-zirconia grit for grind stone and abrasives, alumina-zirconia powder material used for the grit, and furthermore, complex for production of the aforementioned materials, and to provide a method of manufacturing these.

[0002]

[Prior art] The ceramic produced by dispersing ZrO_2 (or $\text{ZrO}_2\text{-Y}_2\text{O}_3$) in Al_2O_3 is referred to as ZrO_2 -toughened Al_2O_3 (ZrO_2 -toughened Al_2O_3) and abbreviated ZTA and is widely used for cutters, etc. because of its high strength and high toughness. For manufacturing ZTA, many different methods are described in "Zirconia ceramics 4", pp. 1-15, a thesis, "Production of ZrO_2 -toughened Al_2O_3 from $\text{Al}_2\text{O}_3\text{-ZrO}_2$ Complex Powder by Vapor-Phase Reaction Method". For example, (1) coprecipitation method, (2) sol-gel method, (3) grinding mill method, (4) melt quenching method, (5) Al-Zr alloy hydrothermal oxidation method, (6) Decomposition of Al-Zr salt mixed solution by ICP (high frequency plasma photoemission device), (7) thermal decomposition of Al_2O_3 slurry containing Zr salt, and (8) vapor-phase reaction method based on the aforementioned thesis can be mentioned.

[0003]

[Problems to be solved by the invention] However, none of the above-mentioned manufacturing

methods of the powder material are adequate. In other words, the coprecipitation method of (1) utilizes $Zr(SO_4)_2 + Al_2(SO_4)_3$ or $ZrCl_4 + AlCl_3 + YCl_3$, etc. as starting raw materials, and an aqueous ammonia, etc. is added dropwise to neutralize and coprecipitate, and handling is made easy, but the powder produced includes neutralized material of Zr, Al and Y independently, and the bonding force is inadequate. In sol-gel method of (2), an alkoxide of aluminum and zirconium is used as the starting raw material, and the raw material is expensive. The mixing by grinding mill method of (3) is a method where uniform mixing is performed for a zirconium material produced by alkoxide method or hydrolysis reaction method and easy-to-calcinate alumina is produced by a grinding mill, but uniformity is limited in comparison to the uniformity achieved by the chemical method. In the melt-quenching method of (4), melting is performed for the starting raw material by a hot-melt furnace, quenching is performed, pulverization is performed to produce essentially an amorphous and uniform powder material, but the method is not suitable for mass production. In Al-Zr alloy hydrothermal oxidation method of (5), the raw material cost is high since $ZrAl_3$, $Zr_5Al_3 + H_2O$ are used. Furthermore, in decomposition of Al-Zr salt mixed solution by ICP method (spray pyrolysis method) of (6), thermal decomposition of Al_2O_3 slurry containing Zr salt method of (7), and vapor-phase reaction method of (8) requires equipment that generates a high temperature such as a frequency plasma photoemission device, thermal deposition device, and vapor generator, and requires an increase in the facility cost.

[0004] Based on the above-mentioned background, the purpose of the present invention is to eliminate the above-mentioned problems and to produce a uniform fine alumina-zirconia ceramic body and alumina-zirconia grit with the high bonding strength of alumina-zirconia, high strength and high toughness, a alumina-zirconia powder material or pulverized material used as the raw material for the above-mentioned materials, complex useful for production of the above-mentioned materials, and furthermore, to provide a manufacturing method thereof.

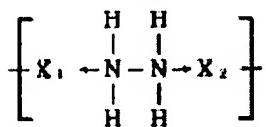
[0005]

[Means to solve the problem] As a result of much research performed by the present inventors in

an effort to eliminate the above-mentioned existing problems, the inventors discovered that the complex produced by the reaction of a raw material comprising aluminum, zirconium and optionally ytterbium with hydrazine in a liquid phase (water, etc.) is very useful, and as a result, the present invention was accomplished.

[0006] In other words, the focus was placed on the hydrazine NH_2NH_2 that forms a two-nuclei complex, and production of the complex comprising the two-nuclei complex formed by coordinate bonding of the hydrazine shown in the following general formula

[Chemical formula 3]



Wherein, X_1 and X_2 are Al, Zr, or Y

and aluminum, zirconium, or ytterbium was performed. The complex in this case means a compound in which the basic unit of two-nuclei complex formed as a result of coordinate bond of hydrazine, aluminum, zirconium, or ytterbium are mutually bonded by metal bonding or coordinate bonding with hydrazine at both ends of aluminum, zirconium, or ytterbium.

[0007] The above-mentioned complex can be easily produced when hydrazine is added to an aqueous solution of a halide of aluminum, zirconium or ytterbium under stirring.

[0008] When calcination is performed for the complex produced as described above after pulverization in an oxidizing atmosphere at a temperature of 300°C or above, a solid solution powder in which aluminum, zirconium or ytterbium are bonded on both ends of the oxygen atom as in the case of Zr-O-Al bond, and when a heat-treatment is performed for the above-mentioned solid solution powder at a temperature in the range of 900°C to 1300°C, an alumina-zirconia powder material can be produced. Furthermore, when die molding is performed for the above-mentioned alumina-zirconia powder material produced followed by HIP treatment, an alumina-zirconia ceramic body can be produced.

[0009] Furthermore, when calcination is performed for the complex after pulverization in an oxidizing atmosphere at a temperature of 300°C or above, and baking is further done at a temperature in the range of 1350 to 1600°C, an alumina-zirconia grit can be produced.

[0010] As a desirable manufacturing method of alumina-zirconia powder material, a method can be mentioned in which drying, pulverizing, and calcinating are performed for the water-washed complex produced by the reaction of a halide of aluminum, zirconium, and ytterbium calculated to form a mixing ratio of 95 to 50 mol% of Al₂O₃, 5 to 50 mol% of ZrO₂, and 1 to 3 mol% of Y₂O₃ for ZrO₂ as the final product with hydrazine in an liquid phase, and baking is further performed at a temperature in the range of 1350°C to 1600°C. In a desirable manufacturing method of an alumina-zirconia ceramic body, classification is performed for the alumina-zirconia powder material produced as described above, die molding is performed and HIP treatment is further performed.

[0011] Furthermore, in a desirable method of manufacturing an alumina-zirconia grit, drying, pulverizing and calcinating are performed for the water-washed complex produced by the reaction of a halide of aluminum, zirconium, and ytterbium calculated to form a mixing ratio of 95 to 50 mol% of Al₂O₃, 5 to 50 mol% of ZrO₂ and 1 to 3 mol% of Y₂O₃ for ZrO₂ as a final product with hydrazine in an liquid phase, and baking is further performed at a temperature in the range of 1350°C to 1600°C.

[0012] Furthermore, it is inexpensive when halides of aluminum, zirconium, and ytterbium, especially, chlorides such as ZrCl₄, AlCl₃ and YCl₃, are used, and production of the target complex can be easily achieved when hydrazine is added dropwise to an aqueous solution produced by mixing the materials in a solvent (water). When a heat-treatment is performed for the above-mentioned complex at a temperature of 300°C or above after pulverization, the bonded hydrazine undergoes a reaction with oxygen in air and releases NH₂ and N₂, and a uniform and rigid Zr-O-Al bond, or a solid solution powder having an oxygen atom bonded with aluminum, zirconium, or ytterbium on both ends can be produced.

[0013] The calculation of the mixing ratio of 95 to 50 mol% of Al₂O₃, 5 to 50 mol% of ZrO₂ and 1 to 3 mol% of Y₂O₃ for ZrO₂ as a final product is based on the reasons given below. In other words, when the mixing ratio of the ZrO₂ is below 5 mol%, the amount of ZrO₂ becomes approximately 4 vol% or below in terms of volume %, and dispersibility of ZrO₂ in the final product is inadequate and rigidity is reduced. On the other hand, when the amount of ZrO₂ used exceeds 50 mol%, the mixing ratio of the ZrO₂ becomes approximately 45 vol%, the dispersing ratio of ZrO₂ is increased, and an increase in the rigidity and strength are insignificant despite an increase in the expensive ZrO₂ used.

[0014] Furthermore, ZrO₂ undergoes a crystal morphology change in the high temperature region, and in order to prevent the problem, addition of an oxide of a rare earth metal such as CaO, MgO, TiO₂, or Y₂O₃ is effective. It is effective to use one or a combination of the above-mentioned stabilizers in the present invention to increase the quality. However, adequate properties can be achieved without the above-mentioned stabilizers when used at room temperature, but it is especially desirable when Y₂O₃ (Y³⁺:0.96A) having a similar Zr and ion radius (Zr⁴⁺:0.82A) and capable of achieving an adequate stability at a small dosage, is used in the present invention. The reason why the amount of Y₂O₃ added is defined at 1 to 3 mol% for ZrO₂ is because an adequate stabilization effect cannot be achieved at an addition of 1 mol% or below, and rigidity is reduced due to a high proportion of cubic crystals with the lesser toughness when 3 mol% or above is used.

[0015] The present invention is explained in further detail according to the process sequence.

[0016] [1] Production of hydrazine complex

(1) Production of aqueous solution

Production is carried out for an aqueous solution of a halide of aluminum and zirconium or furthermore, a halide of ytterbium. For the halides, chlorides, namely, ZrCl₄, AlCl₄, and YCl₄ are used and dissolving is performed in a distilled water to produce an aqueous solution.

Concentration of each of the above-mentioned materials in the aqueous solution is done up to

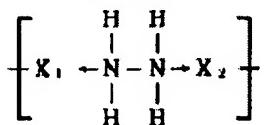
saturation, and in the range of 0.05 to 2 mol% in terms of each oxide is suitable.

[0017] (2) Addition of hydrazine

It is desirable when heating is performed for the aqueous solution to a temperature in the range of 40 to 60°C and addition of hydrazine NH_2NH_2 is slowly performed as the solution undergoes stirring to promote the reaction.

[0018] The precipitate forms a complex consisting of a two-nuclei complex formed as a result of coordinate bonding of hydrazine shown in the following general formula

[Chemical formula 4]



Wherein, X_1 and X_2 are Al, Zr, or Y

and aluminum, zirconium or ytterbium.

[0019] [2] Production of solid solution powder having Zr-O-Al bond

(1) Washing of complex precipitate

It is desirable when a thorough washing is performed to remove the non-reacting material (excess hydrazine, etc.) adsorbed to the complex precipitate and reaction product (NH_4Cl). For convenience, it is desirable when a centrifugal separator is used and washing is done three to five times with hot water of approximately 60 to 80°C.

[0020] (2) Drying of complex precipitate

An appropriate dryer may be used for drying, and for example, a hot-air dryer, vacuum dryer, etc. may be used. Drying is performed as the complex precipitate is spread onto a stainless steel vat to form a thickness approximately in the range of 0.5 to 3 cm, and stationary drying is performed at a temperature below 150°C, and adequate removal of moisture is performed. Furthermore, pelletization is performed by a molding machine such as an extrusion molding machine to form a predetermined shape, and drying is subsequently performed at a temperature of 150°C or below

as well.

[0021] (3) Pulverization and calcination

After drying of the complex precipitate, pulverization is performed by a mortar, universal mixer, ball mill, etc. ahead of time. In order to remove the hydrazine in the complex precipitate, heating is performed for approximately 3 hours at a temperature in the range of 300 to 600°C in an oxidizing atmosphere (atmosphere). The hydrazine undergoes a reaction with the oxygen in air and releases NH₃ and N₂ and forms Zr-O-Al bonds, or a solid solution powder in which aluminum, zirconium or ytterbium are bonded on both ends of the oxygen atom.

[0022] [3] Formation of alumina-zirconia powder material

When a heat-treatment is performed for the solid solution powder in an electric furnace at a temperature in the range of 900 to 1300°C, gamma, theta, alpha-Al₂O₃+m or t-ZrO₂ (includes YO_{1.5} solid solution when ytterbium is used) is produced. Heat-treatment is performed so that crystallization is performed to increase the density of the powder to make handling easy.

[0023] [4] Formation of alumina-zirconia ceramic body

When die molding is performed for the powder material after the heat-treatment and HIP treatment is further performed, alumina-zirconia ceramic body can be produced. It is desirable when the powder material is arranged on a #350 (45 µm) sieve net, die molding is performed for the negative mesh by a die of 50 x 10 x 5 mm under a molding pressure of 100 to 300 MPa, cold isostatic pressure is applied (CIP and molding pressure: 300 to 500 MPa), the molding is vacuum sealed in a heat resistant glass and high temperature hydrostatic pressure (HIP) is applied at 1350 to 1600°C x 1 hour under a pressure of 100 to 300 MPa. The density is promoted in the HIP sintering since isostatic compression is applied, and a ceramic with a higher density can be produced under low temperature in comparison to sintering at ambient pressure.

[0024] [5] Adjustment of alumina-zirconia grit

(1) Pulverization and classification of complex precipitate (complex)

A washed and dried complex precipitate is pulverized and classified by a pulverizer such as roll

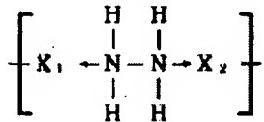
crusher, ball mill and impeller breaker and a sieve mesh such as a vibrating sieve to form, for example, 1 mm or below.

[0025] (2) Calcination, heat-treatment, and baking

In order to remove hydrazine, calcination is performed in an oxidizing atmosphere (atmosphere) at a temperature in the range of 300 to 600°C for approximately 3 hours; then, a heat-treatment was performed by an electric furnace at a temperature in the range of 900 to 1300°C, and finally, when baking is performed under ambient pressure at a temperature in the range of 1350 to 1600°C for 1 to 3 hours, the target grit can be produced. Furthermore, density can be promoted when HIP treatment is performed at the time of baking of the grit as well. [0026]

[Work of the invention] According to the present invention, the complex comprising a two-nuclei complex formed as a result of the coordinate bonding of the hydrazine shown in the following general formula

[Chemical formula 5]



Wherein, X_1 and X_2 are Al, Zr, or Y

and aluminum, zirconium, or ytterbium useful for production of a solid solution powder, alumina-zirconia powder material, alumina-zirconia ceramic body and alumina-zirconia grit is produced, which makes uniform dispersing of the zirconia component possible, and production of a fine alumina-zirconia powder material with excellent bonding property is made possible, and furthermore, production of a alumina-zirconia ceramic body suitable for cutters such as cutting tools with high strength and high toughness, and an alumina-zirconia grit for a wide application is made possible.

[0027] A complex made of a two-nuclei complex, in which the effective ingredient is coordinate bonded with hydrazine is used as a starting raw material; thus, in comparison to the

coprecipitation method, bonding of Zr, Al, and Y is superior, and uniform distribution of zirconia in the final product is made possible, and furthermore, a halide, preferably, a chloride, is used; thus, the cost is low and the manufacturing method is made easy as well.

[0028]

[Working Examples] In the following, the present invention is explained in further detail with working examples.

[0029] Working example 1

Aluminum chloride (AlCl_3) was used as an alumina raw material, zirconium chloride (ZrCl_4) was used as a zirconia raw material, and ytterbium chloride (YCl_3) was used as an ytterbium raw material, and mixing was performed with purified water (deionized water) to form the composition shown in Table I below.

[0030] An aqueous solution with each raw material dissolved in it was heated to 40°C by a mantle heater, 100 ml of hydrazine hydrate [$(\text{NH}_2)_2\text{-H}_2\text{O}$] was slowly added through a separatory funnel of 200 ml in 1 hour under stirring and production of a complex precipitate was achieved. Subsequently, washing was performed for each complex in approximately 70°C hot water four times and removal of non-reacting materials (excess hydrazine) and reaction product (NH_4Cl) was performed by a centrifugal separator. Then, the complex precipitate was arranged on a stainless steel tray to form a thickness of 0.5 cm, drying was performed by a hot-air dryer at 80°C for 2 hours so as to produce a dried product. Furthermore, crushing was performed in a mortar, heating was done in atmospheric air at 350°C for approximately 3 hours so as to produce a solid solution powder of complex precipitate from which hydrazine was removed.

[0031] Subsequently, a heat-treatment was performed for the solid solution powder in an electric furnace at 1200°C for 1 hour and production of $\alpha\text{-Al}_2\text{O}_3 + \text{ZrO}_2$ (includes solid solution: $\text{YO}_{1.5}$) was performed. When an examination was made of the reaction product produced by TEM (transmission electron microscope), uniform dispersing of t-ZrO_2 with a particle diameter of approximately 40 nm among $\alpha\text{-Al}_2\text{O}_3$ with a particle diameter of approximately 0.2 μm was

observed.

[0032] Sieving was performed for the above-mentioned product through a sieve mesh of #350 (45 µm), die molding was performed for the negative mesh with a die of 50 x 10 x 5 mm under molding pressure of approximately 150 MPa, CIP treatment (molding pressure: approximately 400 MPa) was performed, and then, the molding produced was vacuum sealed in a heat-resistant glass. Furthermore, HIP treatment was performed for the above-mentioned molding under a pressure of approximately 200 MPa at 1500°C x 1 hour to produce a sinter.

[0033] For the sinter produced, measurement was performed for density (relative density), Vicker's hardness (JIS Z2244, Vicker's hardness test method), strength (flexural strength: JIS R-1601, Flexural Strength Test Method for Fine Ceramics) and toughness (fracture toughness: KIC: JIS R 1607, Fracture Toughness Test Method for Fine Ceramics). Furthermore, measurement was performed for the crystal size by SEM (scanning electron microscope) and uniformity (distribution state of zirconia in alumina) was verified.

[0034] Furthermore, comparative examples prepared in the same manner and properties of HIP sinter produced according to the coprecipitation method (1) of the prior art (starting raw material: AlCl₃, ZrCl₄, YCl₃, +alkali: ammonia) are shown in Table I below.

[0035] The crystal size of ZrO₂ of the sinters produced as sample No. 1 to 6 is 0.7 µm or less and uniform distribution was achieved as well. Furthermore, high hardness of 17 GPa or above was achieved, flexural strength was at least 500 MPa, and fracture toughness (KIC) was at least 5 MPam^{1/2}.

[0036] The ZrO₂ of sample No. 7 of comparative example is a minimum of 3 mol%, and the amount of ZrO₂ dispersed is low, thus, the strength and toughness are inadequate. On the other hand, the amount of ZrO₂ is high in sample No. 8, thus, uniform distribution is not possible, and despite the high proportion of expensive ZrO₂ added, an increase in quality is not observed. Furthermore, the hardness is 15 GPa or below.

[0037] In sample No. 9, the amount of the Y₂O₃ used as a stabilizer for ZrO₂ was reduced to 1

mol% for ZrO₂, but the hardness is slightly inadequate. On the other hand, the amount of Y₂O₃ was increased to 4 mol% for ZrO₂ in sample No. 10, but cubic phase appears in crystal phase; thus, the toughness is sharply reduced to 4.9.

[0038] In sample No. 11 and 12, production was performed according to a conventional coprecipitation method, but in the manufacturing method, the powder is simply mixed, thus, uniformity is inadequate and sintering density is a minimum of 99%, and in comparison to sample No. 3 and 5 having the same composition, hardness, strength, and toughness are lower.

[0039]

[Table I]

			Working examples					
Sample No.			1	2	3	4	5	6
Composition	Deionized water (ml)	1000	1000	1000	1000	1000	1000	1000
	AlCl ₄	95.6	91.0	81.8	72.3	52.9	53.0	
	ZrCl ₄	4.2	8.6	17.3	26.3	44.6	45.4	
	YCl ₃	0.2	0.4	0.9	1.4	2.3	1.6	
	(NH) ₂ -H ₂ O	100	100	100	100	100	100	
Sinter	Composit ion (%)	Al ₂ O ₃	95	90	80	70	50	50
		ZrO ₃	4.75	9.7	19.4	29.1	48.5	49
		Y ₂ O ₃	0.15	0.3	0.6	0.9	1.5	1.0
	Relative density		99.2	99.4	99.7	99.9	99.9	99.8
	Vicker's hardness (GPa)		20.5	19.0	18.5	17.8	17.2	17.0
	Flexural strength (MPa)		510	590	810	1100	1230	1120
	KIC (MPam ^{1/2})		5.9	6.4	5.2	5.0	7.5	7.2
	ZrO ₂ crystal size (μm)		0.65	0.62	0.42	0.39	0.65	0.65
	Distribution state		Uniform	Uniform	Uniform	Uniform	Uniform	Uniform

			Comparative examples					
Sample No.			7	8	9	10	11	12
Composition	Deionized water (ml)	1000	1000	1000	1000	1000	1000	1000
	AlCl ₄	97.3	42.8	53.2	52.7	81.8	52.9	
	ZrCl ₄	2.6	54.4	48.0	44.2	17.8	44.8	
	YCl ₃	0.1	2.8	0.8	3.1	0.9	2.3	
	(NH) ₂ -H ₂ O	100	100	100	100	*	*	
Sinter	Composit ion (%)	Al ₂ O ₃	97	40	50	50	80	50
		ZrO ₃	2.91	58.2	49.5	48	19.4	48.5
		Y ₂ O ₃	0.09	1.8	0.5	2.0	0.6	1.5
	Relative density		99.2	99.1	99.1	99.1	98.3	98.4
	Vicker's hardness (GPa)		20.5	14.5	15.8	16.2	18.0	15.8
	Flexural strength (MPa)		470	1150	1100	960	700	1050
	KIC (MPam ^{1/2})		4.6	7.0	6.8	4.9	4.8	5.8
	ZrO ₂ crystal size (μm)		0.65	0.80	0.70	0.80	0.70	1.0
	Distribution state		Slightly non- uniform	Slightly non- uniform	Uniform	Uniform	Non- uniform	Non- uniform

*: 6N aqueous ammonia was added until pH 8 was achieved.

Working example 2

Pulverization is performed for the washed and dried materials of sample No. 3 and No. 5 by a roll crusher and sieving and classification were performed by a sieve mesh of a vibrating sieve. Calcination was performed in an atmosphere at 350°C for approximately 3 hours for removal of hydrazine and a heat treatment was performed by an electric furnace at 1200°C for 1 hour and

baking was performed at a temperature of 1500°C for 2 hours under ambient pressure, then, sieving was performed by a sieve mesh of the vibrating sieve to produce a grit with a granularity of #36.

[0040] Production offset stones were produced with the above-mentioned grit produced, and commercial melt-quenched alumina-zirconia grit with ZrO₂:25 wt% (approximately 22 mol%) and 40% type (approximately 36 mol%), and a grinding test was performed against SUS-304. When grinding efficiency of the melt-quenched product ZrO₂:25 wt% type was defined as 100, ZrO₂: 40 wt% type=180, sample No. 3=220, sample No. 5=310 were achieved, and an excellent result was obtained. In this case, uniformity of conventional melt-quenched product is not adequate since at least approximately 5 vol% of the primary crystal of α -Al₂O₃ that exceeds a size of 10 μ m is included in the crystalline in ZrO₂:40% type and at least approximately 50 vol% in 25% type, on the other hand, good uniformity is achieved in the grit of the present invention since the crystal size is low of 1 um or below in α -Al₂O₃ and t-ZrO₂.

[0041]

[Effect of the invention] As described above, the present invention offers a complex of hydrazine useful in production of alumina-zirconia powder material, alumina-zirconia ceramic body and alumina-zirconia grit as well as a manufacturing method for these. Uniform dispersing of effective ingredients is made possible with the complex produced, and a fine alumina-zirconia powder material having a uniform distribution of components and high bonding strength, alumina-zirconia ceramic body having high strength and high toughness, and alumina-zirconia grit with high grinding performance can be easily produced by a simple method, and contribution of the invention to the technical field is significant.

THIS PAGE BLANK (USPTO)